# CAAP Annual Report

Date of Report: *Sept. 30th, 2019*

Contract Number: *DTPH56-16-H-CAAP03*

Prepared for: *U.S. DOT Pipeline and Hazardous Materials Safety Administration*

Project Title: Development of New Multifunctional Composite Coatings for Preventing and Mitigating Internal Pipeline Corrosion

Prepared by: *North Dakota State University*

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For quarterly period ending: *Sept. 30th, 2019*

## Business and Activity Section

### (a) Generated Commitments

Top journal paper published: a journal paper, entitled "*Mechanical, Electrochemical, and Durability Behavior of Graphene Nano-Platelet Loaded Epoxy-Resin Composite Coatings*" was published in a top Journal - Composites Part B: Engineering (Impact factor=6.864). PhD student Xingyu Wang who mainly takes charge of this research was the first author.

Invited talk: Dr. Lin was invited to give a talk, "*Design and Characterization of Functional Nanoengineered Epoxy-Resin Coatings for Pipeline Corrosion Control*", on the national conference of Coating Trends and Technologies 2019 hold in Sept. 10-11, Rosemont, IL.

Conference presentation and papers: Dr. Lin attended and presented their work on high-performance coatings for corrosion control ("*Characterization of Nano-Particle Reinforced Epoxy Coatings for Structural Corrosion Mitigation*"), and machine learning for damage detection and variance identification ("*Data-Driven Identification for Early-Age Corrosion-Induced Damage in Metallic Structures"*) in national conference Bridge Engineering Institute Conference 2019, July 22-25, Honolulu, Hawaii, USA. PhD students, Xingyu Wang and Zi Zhang were the first author of these two papers, respectively.

Conference presentation and paper: PhD student Xingyu Wang attended ASCE Pipeline Conference 2019 hold in July 21-24, Nashville, Tennessee, with a conference paper, entitled, "*Characterization of Graphene Reinforced Epoxy Coatings for Internal Surface of Oil and Gas Pipelines*".

**(b) Status Update of Past Quarter Activities**

The research activities in the 12nd quarter included: (i) Continuing efforts by characterizing new developed nanocomposite coatings in terms of microstructures, mechanical and electrochemical properties; (ii) A comparative study of carbon-based nanofiller nanocomposite coatings and assess their long-term performance; (iii) Flow durability test for modified field performance; and (iv) dissemination of the findings to industry by invited talk and conference presentations, as summarized below.

***Tasks 5-7: Summary of Characterization of the new coating systems and performance assessment***

## 12.1 Objectives in the 12nd Quarter

As presented from the previous study, the nanocomposites showed their potentials to develop high-performance coating as the addition of nanofiller could lead to dramatic improvements on corrosion resistance and mechanical properties. This study continued efforts by characterizing the tribological, mechanical, and electrochemical behavior under long-term performance. Moreover, a flow durability test was designed to quantify modified field performance tests of the developed coatings.

## 12.2 Experimental Study Design

### *12.2.1 Strategy and techniques for experimental research*

The experimental methodology of this project was conducted by parallel tasks: 1) nanofiller reinforcement, 2) polymer screening, and 3) modification of polymer, which were able to understand the mechanism of the developed nanocomposite coatings. The first part was sample preparation, which the procedure of fabricating specimens was provided. After that, the samples were characterized by several microstructural characterization and techniques.

### *12.2.2 Newly employed characterization and analytical techniques*

***a) Electrical equivalent circuit (EEC) technique based on the EIS results***

Based on literature studies, the electrical equivalent circuit (EEC) model was used to interpret the EIS results [7]–[12]. The model was fitted based on the impedance and phase angle curves in the Bode plot. The corrosion phase can be classified into four stages, and each of them is represented by one EEC model, as illustrated in Figure 1.

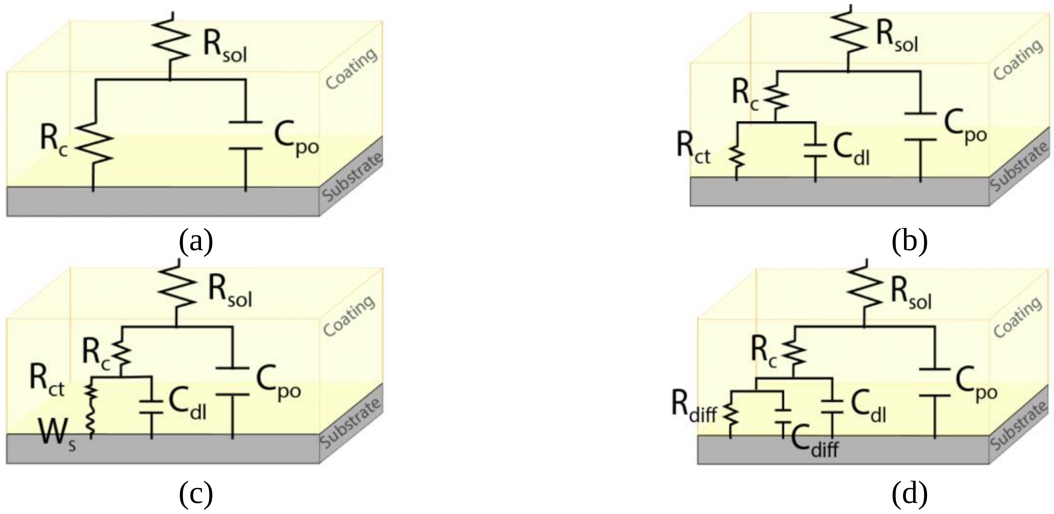



Figure 1. Electrical equivalent circuit models for (a) stage I, model A, (b) stage II, model B, (c) stage III, model B with Warburg element, (d) stage IV, model C

Stage I: Model A was used to present the initial stage, which the coating was an intact film and behave as an isolated protective layer for corrosion protection. At this stage, the equivalent circuit model includes $R_{sol}$ solution resistance, $R_c$ coating resistance, and $C_{po}$ constant-phase element of the coating, indicating the corrosive medium could not penetrate the coating layer.

Stage II: Model B was employed to represent the initial stage of corrosion reaction, while the electrodes were able to penetrate the coating layer to contact with the metal substrate, and the corrosion reaction has been begun. Compared with model A, $R_{ct}$ charge transfer resistance and $C_{dl}$ constant phase element of the double-charge layer were added in the model to simulate the coating-substrate interface.

Stage III: At stage III, Model B with Warburg impedance element ($W$) is included in the electrochemical equivalent circuit when the diffusion effect dominates corrosion. The Warburg element indicates that the electrochemical corrosion reaction in the coating-substrate interface is diffusion-controlled.

Stage IV: The model C can be used to confirm the results, which new parameters of constant phase element of diffusion capacitance ($C_{diff}$) and diffusion resistance ($R_{diff}$) were included. At this stage, severe corrosion damage has occurred and which a thin corrosion product layer was accumulated in the coating-substrate system.

### *12.2.3 A comparative study of carbon-based nanofiller nanocomposite coatings*

In recently, an interesting topic has attracted the authors' attention during the previous experimental and theoretical study. Besides the chemical structures of nanoparticles, researchers believe that the shape of nanoparticles also plays a vital role in the performance of nanocomposites. Our experimental results have confirmed this hypothesis because there were carbon-based nanofillers; hence, carbon nanotube (CNT) and graphene nanoplatelets (GNP), have been studied. Based on transmission electron microscopy (TEM) images, CNT and GNP were characterized as 1-D and 2-D nanomaterials. The incorporation of CNT results in reinforced mechanical properties, and improved corrosion resistance can be observed in the nanocomposite with GNP. To further study the various improvements that attributed by the shapes of nanofillers, another type of carbon-based nanoparticle, hence, Fullerene-C60 was introduced in this project. Similar to CNT and GNP, Fullerene-C60 is a commonly used nanofiller that contains only carbon atoms. In order to compare with the nanocomposites that reinforced by CNT and GNP, a similar experimental design was used to evaluate the performance of Fullerene-C60 reinforced epoxy, which was explained in the following section.

### *12.2.4 Flow durability test for modified field performance*

As proposed in the project description, long-term performance was planned to evaluate the reliability and durability of the developed coatings. The designed accelerated flow instrument contained a liquid reservoir, a pump, and a flow channel. The test samples were first mounted in the channel. With the adjustable flow speed provided by the pump, the design was used to simulate the condition of the internal surface of pipelines.

## 12.3 Results and Discussion

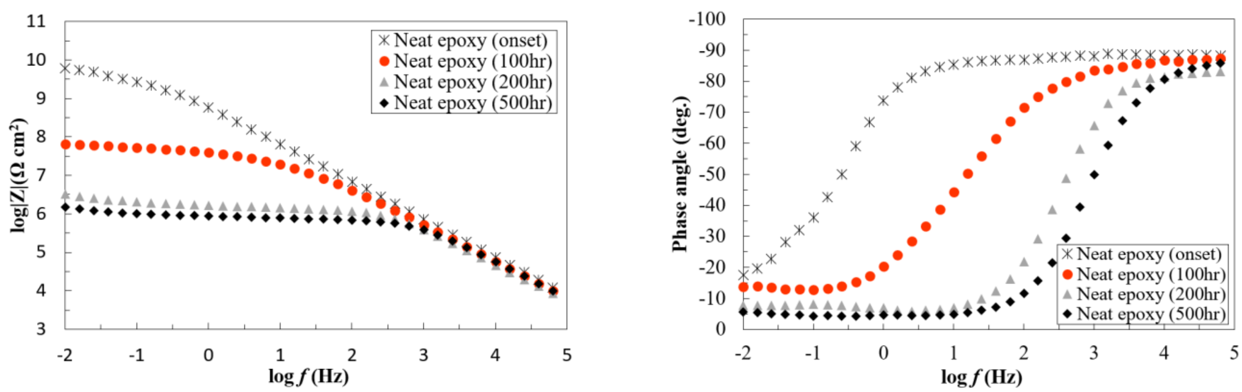
### *12.3.1 Nanofiller reinforced nanocomposites*

Test results for nanofiller reinforcement were presented in this section, which included both characterization and performance of the nanocomposite coatings containing varied weight content nanoparticles.

**(a) Neat epoxy**

The results of the neat epoxy group were employed as a reference for all the nanofiller coatings, as typical degradation process was observed in the samples during the Salt fog test. A typical degradation process of a coating film should be observed from both impedance and phase angle curve in the Bode plots.

Subsequently, the electrical equivalent circuit (EEC) model could be determined by interpreting the impedance and phase curves. The EEC model could also be used to demonstrate the degradation process of the neat epoxy coating. At the fresh stage, model B with Warburg impedance element (W) was introduced to fit the EIS data. It appeared that there were diffusion paths for the electrolyte to reach the coating-substrate interface and initiated coating degradation. After 500 hours of exposure, model C was suitable for the neat epoxy sample due to the accumulated corrosion products at the coating-substrate interface.




(a) (b)

Figure 2. Impedance curve (a) and phase angle curve (b) of the neat epoxy group

**(b) CNT/epoxy nanocomposites**

As shown in Fig. 3, the exposure time elapsed and the accumulated corrosion products formed a thin film on the substrate surface. Slight decreases of impedance modulus were observed for the coating with low content of CNT (0.1 and 0.5 wt.%). All the CNT/epoxy groups reached to stage IV (model C) at 500 hours exposure due to the accumulated corrosion products.

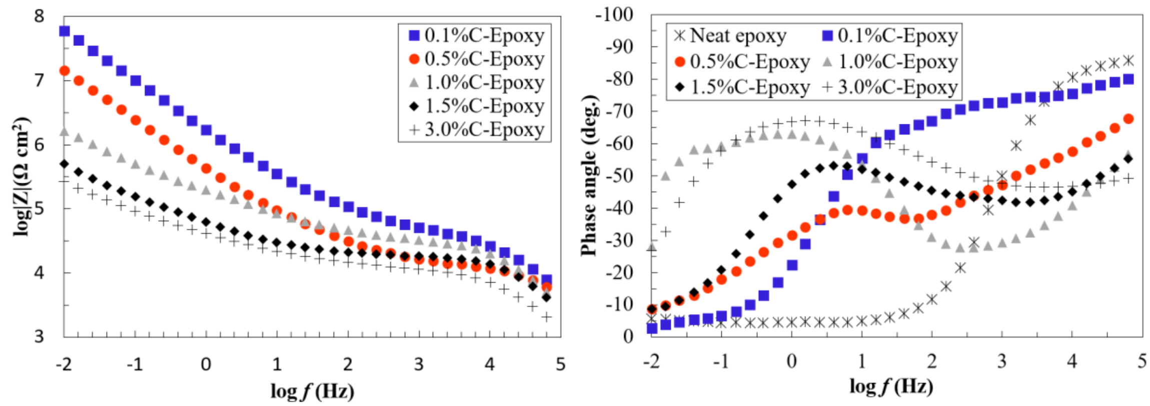



Figure 3. Phase angle curve of the CNT/epoxy before exposure (a) and after 500 hours (b).

**(c) GNP/epoxy nanocomposites**

As illustrated in Figure 4, among all the GNP/epoxy coatings, the group 0.1, 0.5 and 1.0%G-epoxy exhibited the best performance in terms of significant improvements of durability. With a slight decrease in the impendence modulus at 0.01 Hz, suggesting that the coating film with 0.1 to 1.0 wt.% GNP content still provided an effective barrier for the substrate after the 500-hour exposure.

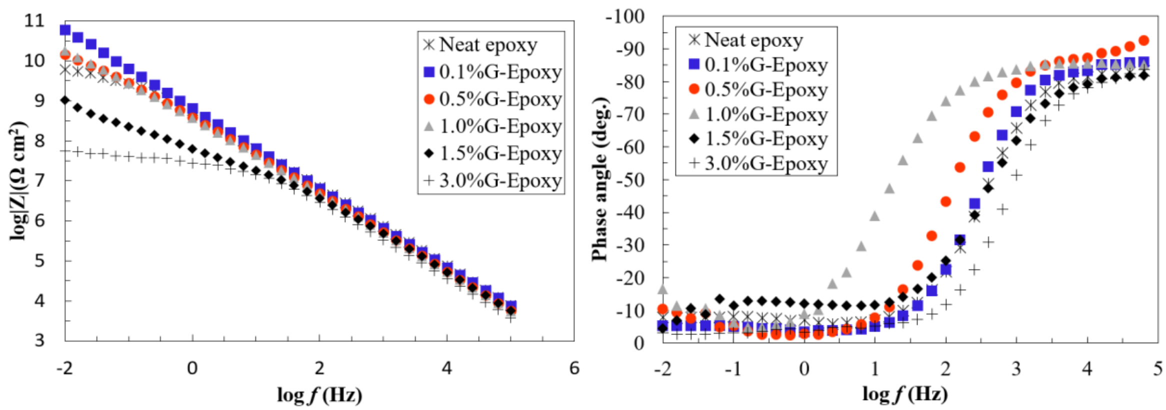
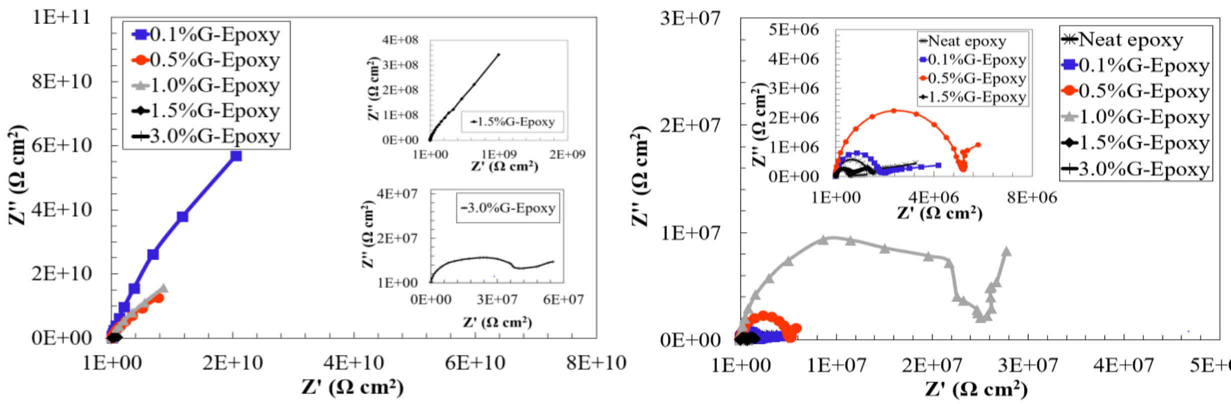



Figure 4. Phase angle curve of the GNP/epoxy before exposure (a) and after 500 hours (b).

EIS data were interpreted as four stages as listed in Table 1 and plotted in Fig. 5 in in Nyquist in accordance with the equivalent electrical circuit models. Clearly, the information collected from Table 1 and Fig. 5 matched well with the observation in Fig. 4. Groups, 0.1%G-Epoxy, 0.5%G-Epoxy, and 1.0%G-Epoxy, remained at Model A at the initial stage, and then reduced to the second stage, Model B, shown in Table 1, indicating that a very small amount of a graphene nanofillers could effectively improve the barrier property of the composite coatings and then enhance their long-term performance. Table 1 also demonstrated that the samples coated by the neat epoxy, 1.5%G-Epoxy or 3.0%G-Epoxy stayed in the third stage, Model B with W, where the coating had less effective barrier protection against corrosion occurring at the coating-substrate interface. Although the equivalent electrical circuit models or Nyquist plots could not accurately capture the level of severity when exposure time increased from 100 to 200 hours, the information was still sufficient to distinguish the neat epoxy, 1.5%G-Epoxy and 3.0%G-Epoxy from the other coated samples. As shown in Table 1, the samples reached to the fourth stage, Model C, when exposed after 500 hours, where these samples exhibited the semi-circuit curve in Nyquist plot and the lowest impedance values in the low frequency region of Bode plot.

**Table 1** EIS data associated with different stages of the equivalent electrical circuit models.

| Label | Content of graphene (wt.%) | Exposure to accelerated environmental stresses | | | |
|---|---|---|---|---|---|
| | | Onset | 100-hr | 200-hr | 500-hr |
| Neat epoxy | / | Model B with W | Model B with W | Model B with W | Model C |
| 0.1% G-Epoxy | 0.1 | Model A | Model B | Model B with W | Model B with W |
| 0.5% G-Epoxy | 0.5 | Model A | Model B | Model B | Model B with W |
| 1.0% G-Epoxy | 1.0 | Model A | Model B | Model B | Model B with W |
| 1.5% G-Epoxy | 1.5 | Model B with W | Model B with W | Model B with W | Model C |
| 3.0% G-Epoxy | 3.0 | Model B with W | Model B with W | Model B with W | Model C |




(a) impedance curves at onset stage

(b) phase angles after 500-hr exposure

Figure 5. Nyquist plots for the test samples: (a)-(d)

## 12.4 Dissemination of project results

### *12.4.1 Invited talk to the national conference for the coating industry*

The PI Dr. Lin was invited to give a talk, entitled "*Design and Characterization of Functional Nanoengineered Epoxy-Resin Coatings for Pipeline Corrosion Control* ". in the recent conference, **Coating Trends and Technologies 2019**, at Rosemont, IL, Sept. 10-11, 2019, where he presented the group study on the new coating development and characterization for oil/gas pipeline corrosion control (in his presentation slides with acknowledgment to the USDOT CAAP supports, see *Figure 55*).

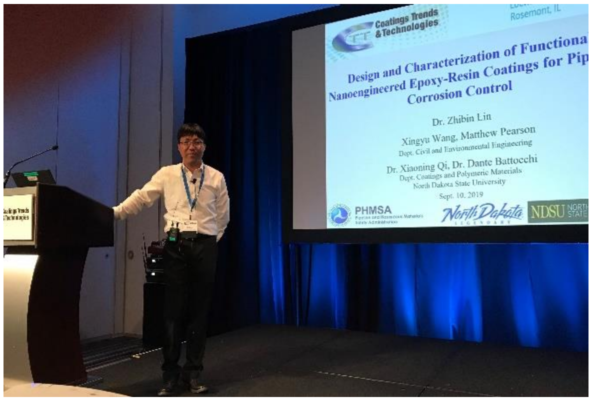



Figure 6 Dr. Lin gave an invited talk on the national coating conference in Rosemont, IL, on Sept. 10$^{th}$, 2019

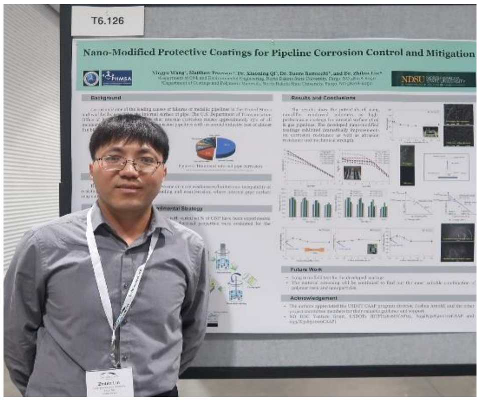



Figure 7 Dr. Lin attended and presented the poster sections in World Techconnect 2019 in Boston, MA, on June 17-19, 2019.

### 12.4.2 National conference presentation and poster

Dr. Lin attended and presented their work on the poster sections for high-performance coatings in national conference World Techconnect 2019 in Boston, MA, on June 17-19, 2019 (see *Figure 56*). PhD student Xingyu Wang attended and presented his work in the ***ASCE Pipeline Conference 2019*** hold in July 21-24, Nashville, Tennessee with a conference paper, entitled, "*Characterization of Graphene Reinforced Epoxy Coatings for Internal Surface of Oil and Gas Pipelines*". Dr. Lin attended and presented their work on high-performance coatings for corrosion control in national conference Bridge Engineering Institute Conference 2019, July 22-25, Honolulu, Hawaii, USA. The presented work included "*Characterization of Nano-Particle Reinforced Epoxy Coatings for Structural Corrosion Mitigation*", and "*Data-Driven Identification for Early-Age Corrosion-Induced Damage in Metallic Structures"*. The information exchange on high-performance coatings during these dissemination activities raised great attention from audience in industry (from coating materials to inspections) and several companies directly contacted Dr. Lin to show their interest for potential collaborations.

### 12.4.3 High school student outreach program

As stated in the last report, the major efforts in this project was to recruit high-school students each summer to work in the pipeline research and foster their interest in this field. In this summer, Dr. Lin's group recruited two high school students, Isak Harmon and John Goeres, from North Dakota Governor's Schools program (see Fig. 57). These two students worked with the graduate students Muhammad Metla, Zi Zhang and Matthew Pearson by participating in the USDOT PHMA to learn the nanoparticle modified coating synthesis, and the corrosion behaviors of metallic materials. This outreach could motivate them to pursue the pipeline safety and corrosion control area in their future career.

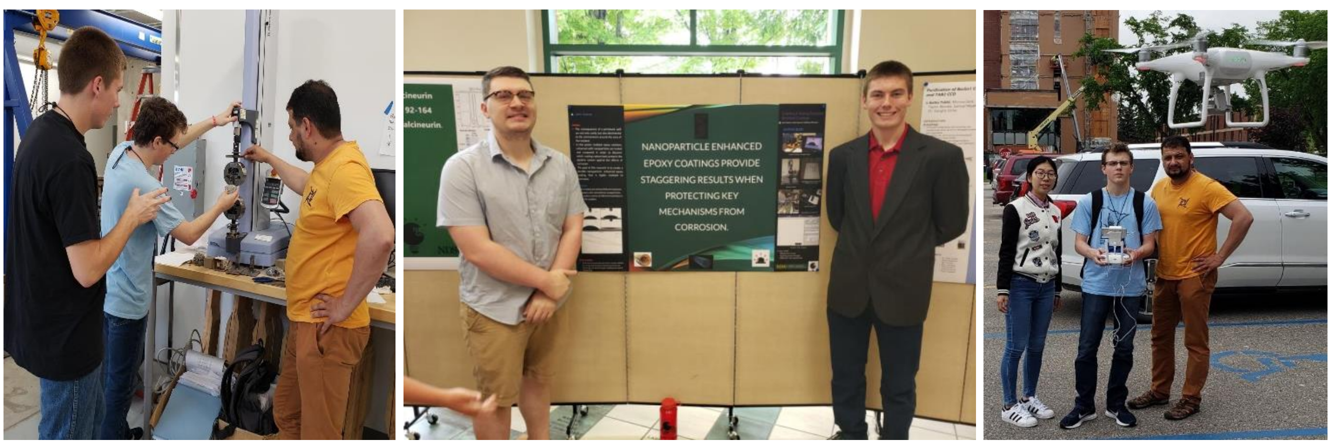



Figure 8 Students working at the outreach program: Muhammad Metla, Isak Harmon, John Goeres, Matthew Pearson, and Zi Zhang

**(e) Description of any Problems/Challenges**
No problems are experienced during this report period

**(f) Planned Activities for the Next Quarter**
The planned activities for next quarter are listed below:

- The modified field reliability test with liquid flow instrument was used to simulate the environment of the internal surface of a pipeline.
- The authors will continuously study to evaluate and improve the overall performance of the proposed coating.